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Research paper

# Nitrogen losses, use efficiency, and productivity of early rice under controlled-release urea

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ABSTRACT

Ammonia ($NH_3$) volatilization and nitrogen (N) surface runoff from rice (*Oryza sativa* L.) paddies contribute to air and water pollution in China and everywhere else. The purposes of this study were to assess N losses through $NH_3$ volatilization and surface runoff and to determine the grain yield and N use efficiency (NUE) of early rice in double rice cropping system in southern China. We implemented six treatments viz., control with 0 kg N $ha^{-1}$ (CK), basal application and split application (1/2 at transplanting, 1/4 at tillering, and 1/4 at panicle stages) of urea (U), and basal applications of three controlled-release urea (CRU) sources (polyurethane-coated urea [CRU-1], degradable polymer-coated urea [CRU-2], and water-based polymer-coated urea [CRU-3]) all applied at 165 kg N $ha^{-1}$. Results showed that CRU-1 and CRU-2 significantly reduced $NH_3$ volatilization (23 to 62%) and N surface runoff losses (8 to 58%) compared with U. Precipitation and ammonium-nitrogen ($NH_4$-N) concentration in surface water from rice paddy were predominant factors defining N losses through $NH_3$ volatilization and surface runoff. Application of CRU reduced $NH_4$-N concentration and pH of surface water and N losses through surface runoff. The CRU produced similar (−3 to 4%) or higher (5–16%) rice grain yields and increased NUE (3 to 34%) and N uptake (3–55%) compared with U. Polymer-coated urea can reduce environmental risks of N losses through volatilization and surface runoff while maintaining rice yield and N uptake, it also enhances NUE compared with urea in double rice cropping system in southern China.

## 1. Introduction

Agricultural practices not only determine crop productivity, but also largely influence the global environmental quality (Tilman et al., 2002). To feed the escalating population, modern agriculture in East Asia, especially China, is highly intensive and productive, which can be attributed to the use of new technologies and new crop varieties, and the high inputs of nitrogen (N) fertilizer and pesticide (Xiong et al., 2008). Unfortunately, excessive N inputs in intensive agricultural ecosystems have resulted in decreased N use efficiency (NUE), as well as increased N loss to the environment, polluting air and water systems through ammonia ($NH_3$) volatilization, surface runoff, leaching and denitrification (Zhu and Chen, 2002; Galloway et al., 2008; Xue et al., 2014; Zhao et al., 2015).

Rice (*Oryza sativa* L.) is one of the most important staple foods, feeding over half of the global population (Van Nguyen and Ferrero, 2006). China contributes approximately 28% of the global rice production on approximately 19% of the world's rice planting area in 2014 (FAO, 2014), mainly due to the wide adoption of double rice cropping system in southern China (Wu et al., 2013). In these regions, solar radiation, temperature, and precipitation are suitable for multiple cropping (Hu et al., 2015). However, the area of double rice cropping system has already dropped from 66% in 1980s to 40% recently due to labor shortage, low grain yield and negative economic returns (MOA, 2015; Wu et al., 2013; Wang et al., 2017). In addition, climate change and other multiple cropping systems might have contributed to this change (Hu et al., 2015). The double rice cropping region of southeast Hubei province is a typical subtropical humid monsoon region that is vulnerable to climate change (Deng et al., 2015). In the region, the early rice growing season extends from April to July and corresponds with the plum rain period (the East Asian rainy season) in the middle and lower reaches of Yangtze river (Guo et al., 2017). Recently, extreme weather events caused by climate change, such as high temperature, storms, floods, etc. (Mohanty et al., 2013) have frequently occurred in

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early rice growing season. The lower grain yield of early rice compared to late rice was mainly restricted by varietal and climatic differences (including temperature and precipitation during the vegetative and reproductive period) (Qin et al., 2013; Wang et al., 2017). During the vegetative period, low temperature decreases the crop growth, while high frequency precipitation hinders the topdressing and increases the risk of N runoff and leaching (Ji et al., 2007; Huang et al., 2011; Wang et al., 2017).

The average NUE for rice is 30 to 35% and approximately 50% N is lost to the environment (Zhu and Chen, 2002). Among the various reactive N losses under rice, $NH_3$ volatilization and N surface runoff are the main contributors to air and water pollution in China (Chen et al., 2014; Li et al., 2017a). Ammonia volatilization is an important pathway for N loss under rice (De Datta, 1987; Zhu and Wen, 1992), ranging from 10 to 50% of the 19.2 million tons of N fertilizer applied annually in global rice systems (Coskun et al., 2017). It may account for 10 to 80% of the total reactive N loss (De Datta et al., 1990; Griggs et al., 2007). Atmospheric $NH_3$ is an important air pollutant, contributing to acidification, eutrophication and loss of biodiversity in natural and semi-natural ecosystems (Bouwman et al., 2002). The majority of volatilized $NH_3$ from rice systems is returned to agroecosystem by dry or wet deposition. High amounts of volatilized $NH_3$ produce high deposition (Xie et al., 2008; Wang et al., 2016b). In addition, $NH_3$ secondary deposition indirectly produces nitrous oxide emissions, leading to global warming (Katata et al., 2013; Hube et al., 2017).

Although N loss through surface runoff occurs to a lesser extent, Zhu (2000) reported that N loss through drainage and surface runoff under rice accounted for 3 and 6% of the applied N fertilizer (345 kg N $ha^{-1}$ $yr^{-1}$), respectively, which ranged from 20 to 23% of the total N losses under rice (Chen et al., 2014; Li et al., 2017a). Generally, mineral N is highly soluble in water and readily lost via surface runoff and leaching because of unpredictable or persistent rainfall immediately after irrigation or N fertilization (Ji et al., 2007; Zhang et al., 2010). However, N leaching is typically not identified to be an important N loss pathway under rice due to the limited water permeability and long-term flooded condition in fine-textured soils (Liang et al., 2014). Numerous studies have shown that after applying urea, the $NO_3$-N concentration in surface water and leachate was much lower than that of $NH_4$-N concentration (Ji et al., 2007; Yang et al., 2013b). The N loss due to leaching during the double rice cropping system accounted for 0.7–2.3% (average 1.5%) of the total N applied (300 kg N $ha^{-1}$) (Ji et al., 2011). Accordingly, better N management strategies are needed to reduce environmental risk and obtain relatively high yields and NUE in rice.

Even though conventional N management strategies such as split N application and N deep placement reduce N losses and increase NUE (Gaudin, 2012; Liu et al., 2015), lack of matching machinery and effective agricultural labor forces often limit the application of these strategies (Zhang, 2008). Recently, controlled-release urea (CRU), as a new, effective and environmentally friendly fertilizer, has been extensively applied to rice, wheat (*Triticum aestivum* L.), maize (*Zea mays* L.) and other field crops (Wilson et al., 2009; Kiran et al., 2010; Connell et al., 2011; Wang et al., 2013, 2016a; Xu et al., 2013; Zhao et al., 2013). Furthermore, CRU is a preferred alternative to conventional urea as it has many advantages including labor and time savings due to the single basal application, higher NUE, and N release rate synchronized with plant N uptake, and lower N losses under heavy rainfall or irrigation (Trenkel, 1997; Shaviv, 2001). Many studies have demonstrated that CRU significantly improved NUE and reduced N losses through volatilization and surface runoff (Ji et al., 2007; Golden et al., 2009; Xu et al., 2013; Fageria and Carvalho, 2014; Li et al., 2017a). It has been shown that CRU reduces N losses under rice due to lower $NH_4$-N concentrations in the soil and in soil solution compared with conventional urea (Xu et al., 2012; Yang et al., 2013a; Li et al., 2017a). In the context of China's zero fertilizer growth plan, CRU offers a superior option to enhance NUE and minimize environmental pollution.

Polymer-coated urea (PCU) is the most promising CRU due to its excellent controlled release effect (Ye et al., 2013; Shen et al., 2015). Several PCU fertilizers coated with polyurethane, degradable polymer and water-based polymer have been applied widely in recent years as these are non-toxic, less costly, and environment friendly (Beres et al., 2012; Chen et al., 2013; Shen et al., 2015; Guo et al., 2016). Nonetheless, few studies have compared the effect of different PCU fertilizers on N losses, NUE, and N uptake in double rice cropping system in southern China (Xu et al., 2013; Li et al., 2017a). Our previous report has indicated that there was considerable variation in the benefits of CRU with regard to reducing $NH_3$ volatilization and N surface runoff (Li et al., 2017a). Since the release pattern of CRU was affected by soil temperature and moisture (Grant et al., 2012; Ke et al., 2017), and the climatic characteristics of early rice and late rice were significantly different, it was necessary to separately evaluate the performance of CRU in early rice and late rice. The main purposes were 1) to compare the effects of three PCU fertilizers on N losses (via $NH_3$ volatilization and surface runoff), NUE and early rice yield, and 2) to screen optimal PCU fertilizers for reducing N losses while increasing NUE and yield of early rice, compared with conventional urea in southern China.

## 2. Materials and methods

### 2.1. Site description

Two field experiments were conducted in Wuxue County, Hubei Province, China. One located in Dajin Town (29°59′N, 115°38′E) in 2013 and the other located in Meichuan Town (30°7′N, 115°36′E) in 2014 during early rice growing season in double rice cropping system (Fig. 1). The previous crop was winter rapeseed for the field used in 2013, and was winter fallow for the field used in 2014. Wuxue county is located in the southeast Hubei province and has a typical subtropical humid monsoon climate in the center of the Yangtze River Valley. The average annual air temperature at Wuxue county is 17.1 °C and the average annual precipitation is 1456.3 mm (1981–2010). During the early rice growing season (Fig. 2), the average daily air temperature and total precipitation were 26.8 °C and 255.7 mm in 2013 (May 11th–July 26th), and 24.8 °C, and 591.9 mm in 2014 (May 1st–July 22th).

Prior to field operations, soil samples were collected to a depth of 20 cm at 15 randomly selected points from each site and the samples were pooled into a single sample per site. The two soils were classified as Alfisol (Soil Survey Staff, 1999). The initial soil properties of plough layer (0–20 cm) before the experiment began in 2013 and 2014 were presented in Table 1.

### 2.2. Experimental design and statistical analysis

Field experiments were arranged in a randomized complete block design with three replicates of six treatments: control with 0 kg N $ha^{-1}$ (CK), basal application of urea ($U_b$), split application of urea ($U_s$), and three basal applications of CRU (CRU-1, CRU-2 and CRU-3). Nitrogen fertilizers in all treatments (excluding CK) were applied at 165 kg N $ha^{-1}$. All CRU fertilizers and urea (46% N) in the $U_b$ treatment were broadcasted in a single dose at transplanting. Urea in the $U_s$ treatment was broadcasted in three applications, with 1/2 at transplanting, 1/4 at tillering and 1/4 at panicle stages. Phosphorus and K fertilizers in all treatments were applied at transplanting in a single dose of 75 kg $P_2O_5$ $ha^{-1}$ (single superphosphate, 12% $P_2O_5$) and 75 kg $K_2O$ $ha^{-1}$ (potassium chloride, 60% $K_2O$), respectively. The three CRU fertilizers used in this study were polyurethane-coated urea (CRU-1, Light blue, 44% N), degradable polymer-coated urea (CRU-2, Blue, 44.8% N) and water-based polymer-coated urea (CRU-3, White, 41.4% N). They were produced by Agrium Advanced Technologies, Inc., China Agricultural University and the Chinese Academy of Soil Sciences in Nanjing, respectively (Li et al., 2017a). The individual plot area was

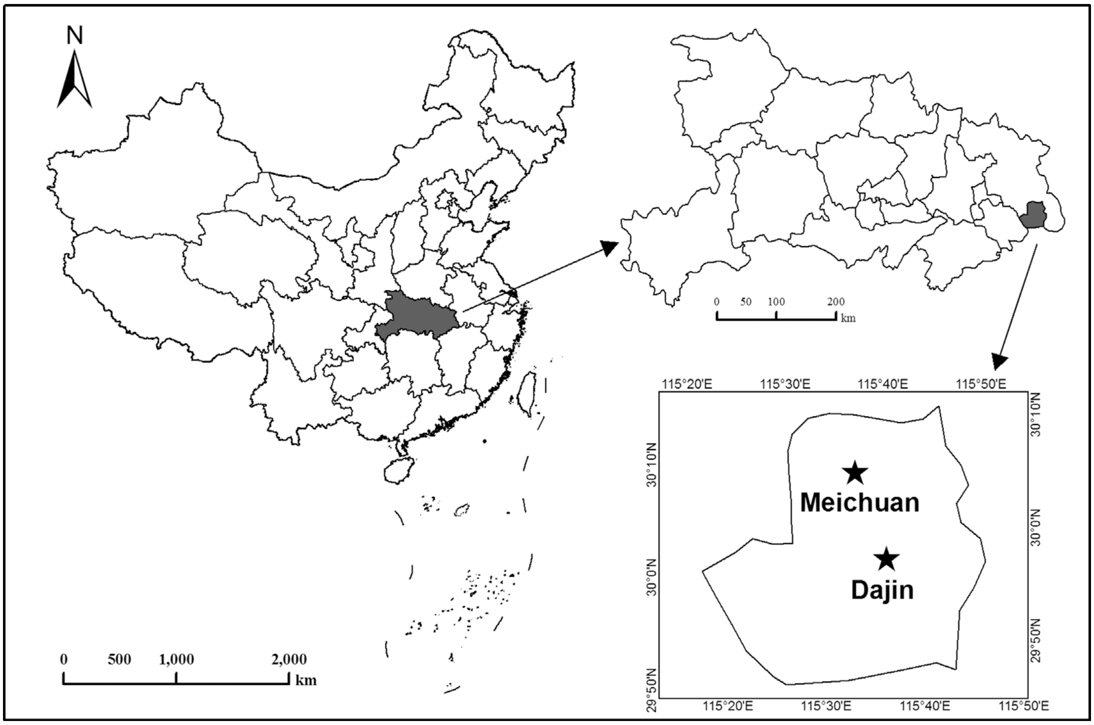


**Fig. 1.** Location of experiment field site.

20 m$^2$ and each plot had an inlet and outlet for irrigation and drainage. Individual plots were bordered with plastic film inserted to a depth of 30 cm below the soil surface (30 cm wide at the base and 20 cm high on both sides of the ridges) to prevent seepage between adjacent plots.

An *indica* conventional rice cultivar (E Zao 18) was used in this study. Rice seedlings were transplanted with 3 seedlings per hill in both years and the planting space was 0.20 × 0.18 m. The respective basal fertilizer application, first and second topdressings of N fertilizer, and harvesting were done on 11 May, 21 May, 20 June, 26 July in 2013, and 1 May, 18 May, 19 June, 23 July in 2014, respectively. All plots were immediately furrow irrigated after transplanting. There were eight drainage events in 2013 and six in 2014. After each rain event, if the water depth exceeded 6 cm in the paddy field, plots were drained to maintain the water depth between 3 and 5 cm. During the mid-season aeration, water was drained from each plot. The time of mid-season aeration should be carried out at the end of the tillering stage to panicle initiation stage (about 30 days after rice transplanting). The durations of mid-season aeration were from 10 June to 18 June in 2013 and from 2 June to 19 June in 2014, respectively. This practice is the common water management for rice in China because it promotes the growth of tillers, removes toxic substances, and improves root growth. After the mid-season aeration, plots were irrigated and no irrigation was applied afterward, until crop harvest. All plots were drained at approximately 10 d before harvest. Other field practices, such as tillage, weeding and spraying pesticide, were managed by local traditional farming practices.

Data were analyzed statistically using GenStat 18th Edition (VSN International Ltd., Hemel Hempstead, UK). Treatment was considered as the fixed effect, date of sampling as the repeated measure variable, and replication as the random effect. When treatments, sampling date, and their interaction were significant, means were separated by using the least significant difference (LSD). Relationships between $NH_3$ volatilization rate and surface water properties, and between mineral N surface runoff and precipitation were analyzed using the Pearson correlation. Statistical significance was evaluated at $P < 0.05$. Figures were plotted with OriginPro 9.0 software (OriginLab USA).

### *2.3. Sampling and measurement*

#### *2.3.1. Ammonia volatilization, surface water runoff*

Ammonia volatilization was determined by a vented-chamber method with two chambers in each plot (Wang et al., 2004). The chamber (Fig. 3) was made of polyvinyl chloride tube (height 30 cm and diameter 16 cm) with two pieces of phosphoglycerol soaked sponges. Samples were collected daily after fertilization, followed by 2–3 d intervals for another week, and then at a weekly interval until the rice harvest. Ammonia absorbed in the lower sponges were extracted with 300 mL of 1.0 mol L$^{-1}$ potassium chloride solution after 1 h oscillation. Ammonium quantities in the extracted solutions were analyzed by the indophenol blue colorimetric method using an ultraviolet-visible spectrophotometer at a wavelength of 625 nm (UV-5200, METASH). The $NH_3$ volatilization flux was calculated as described by Xu et al. (2012).

Daily precipitation and air temperature (maximum, minimum and mean values) were recorded from the weather station (CR800, Campbell, USA) located within 1 km from the Wuxue experimental site. Surface water samples (Fig. 3) were collected from five randomly chosen locations within a plot using an injector; the samples were placed on ice in a container for transport to the laboratory (Shang et al., 2014). Drainage water was collected after each intensive rainfall event, the mid-season aeration, and the terminal drainage before harvest. The depth of surface water was measured at five locations per plot to calculate runoff volume using volume-depth relationships before and after each runoff event. Mineral N concentration and pH of all water samples were measured as described by Li et al. (2017a). Mineral N surface runoff loss was calculated as described by Wang et al. (2015).

#### *2.3.2. Measurements of nitrogen release from controlled-released urea, grain yield and N uptake*

Nitrogen release characteristic of CRU was determined in the other field near the experimental plot using a buried bag-weight method (Wilson et al., 2009; Xu et al., 2013; Yang et al., 2013b). Thirty double-layered (1.0 mm mesh size) mesh bags (5 × 5 cm) containing CRU fertilizers (10.0 g) were buried about 5–10 cm depth in the soil before

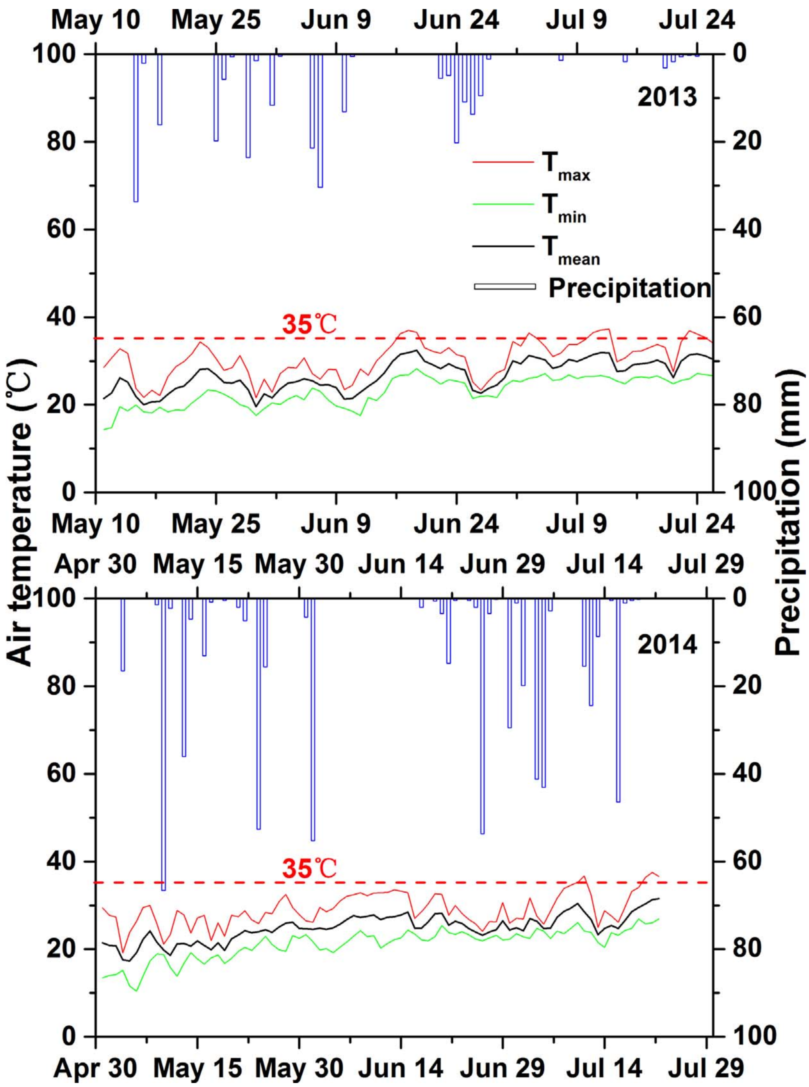


**Fig. 2.** The air temperature (maximum temperature, $T_{max}$; minimum temperature, $T_{min}$; mean temperature, $T_{mean}$) and daily precipitation during the 2013 and 2014 rice growing seasons.

rice transplanting. Three bags were randomly removed at ≈10 d intervals until the rice harvest, cleaned with de-ionized water to remove soil particles, and then placed to the lyophilizer for drying 2–3 d at −50 °C (Labconco FreeZone, 6 L, USA). The loss of weight from CRU calculated as the difference between initial and final weights was considered as the percent of N released from CRU; the moisture content of the coated material was negligible and accounted for approximately only 1.0% in the loss-of-weight calculation.

At harvest, rice grain yield was measured from 10 $m^2$ area in each plot using hand harvest and machine threshing. Rice plant samples were collected from 6 ridges per plot, divided into straw and grain components. All plant samples were oven-dried at 60 °C to a constant weight, then weighted and analyzed for total N concentration using $H_2SO_4$-$H_2O_2$ digestion and a continuous-flow injection analyzer (AA3, Bran and Luebbe, Norderstedt, Germany) (Bao, 2000). Total N uptake in rice plants was calculated by multiplying total N concentration in the straw and grain by their biomass. The apparent recovery N use efficiency (NUE) was calculated using Eq. (1) (Silveira et al., 2007):

$$NUE\,(\%) = \frac{N_{uptake}\ (\text{N applied treatment}) - N_{uptake}\ (\text{control treatment})}{\text{Total N fertilizer applied}} \times 100 \qquad (1)$$

## 3. Results

### 3.1. Nitrogen release of controlled-release urea

Nitrogen release of CRU products were significantly affected by the different coating materials (Fig. 4). During a 10-d interval, N release rates were 48.7, 39.7, and 71.7% of fertilizer N concentration for CRU-1, CRU-2 and CRU-3 in 2013, and 28.4, 24.8, and 83.2% in 2014, respectively. About 70 to 85% of total N was released from all fertilizers at 75 d after transplanting. Nitrogen release was greater for CRU-3 than either CRU-1 or CRU-2 (Fig. 4).

**Table 1**
The initial soil properties of plough layer (0–20 cm).

| Year | Site | pH | Organic C (g $kg^{-1}$) | Total N (g $kg^{-1}$) | $NH_4$-N (mg $kg^{-1}$) | $NO_3$-N (mg $kg^{-1}$) | Olsen-P (mg $kg^{-1}$) | $NH_4OAc$-K (mg $kg^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 2013 | Dajin | 4.9 | 19.1 | 1.4 | 3.0 | 2.4 | 7.2 | 106.2 |
| 2014 | Meichuan | 6.2 | 22.3 | 1.8 | 6.8 | 3.2 | 8.2 | 51.0 |

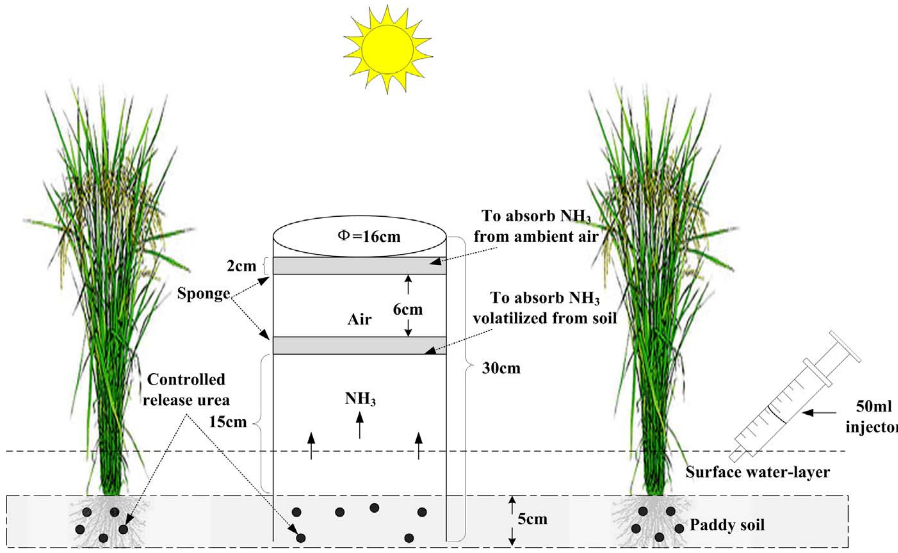


**Fig. 3.** Schematic view of capturing ammonia volatilization and collecting water samples from paddy soil.

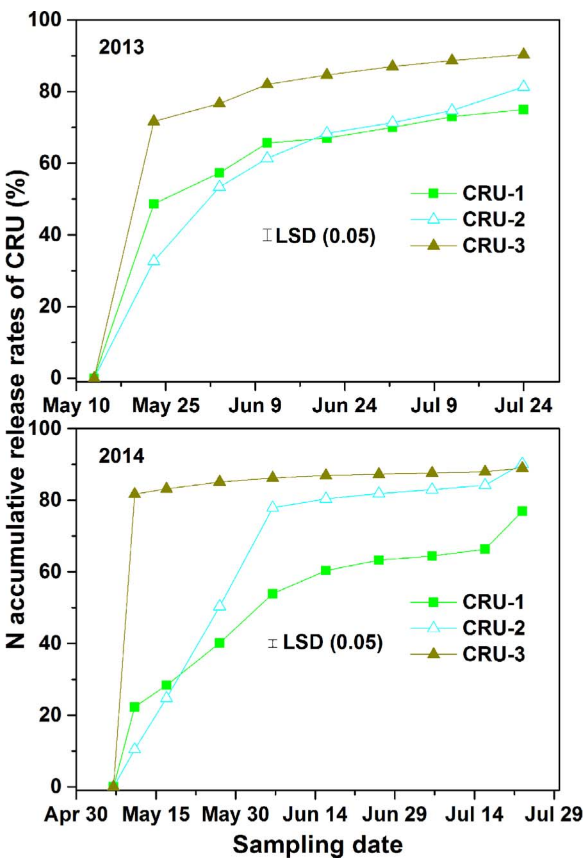


**Fig. 4.** Accumulative release rates of N for controlled-release urea (CRU) under field condition during the 2013 and 2014 rice growing seasons. LSD (0.05) is the least significant difference among treatments in a sampling date at $P < 0.05$. CRU-1, polyurethane-coated urea; CRU-2, degradable polymer-coated urea; CRU-3 and water-based polymer-coated urea.

### 3.2. Surface water ammonium-nitrogen concentration and pH

The surface water $NH_4$-N concentration varied significantly with the type of N fertilizers (Fig. 5a, b). In the $U_b$ treatment, the surface water $NH_4$-N concentration peaked between 4 and 6 d after application of the basal N fertilizer and rapidly dropped to similar level as for CK treatment after about 20 d. Three obvious peaks were identified between 1 and 6 d after application of the basal N fertilizer and two topdressings in the $U_s$ treatment. The surface water $NH_4$-N concentration of the CRU peaked at 14 d after application of the basal N fertilizer and rapidly dropped to similar level as for CK treatment after about 30 d in 2013; but few perceptible $NH_4$-N peaks were detected in the CRU and CK treatments in 2014, which were far lower 46.0–94.9% than that of the U treatments.

The surface water pH values ranged between 5.57–8.77 and 6.61–8.29 in 2013 and 2014, respectively. These values were higher than those determined in the rice arable soil layer (4.93 and 6.17 in 2013 and 2014, respectively) prior to transplanting (Fig. 5c, d). Compared with the U treatments, the CRU treatments decreased the average pH values by 0.10–0.36 and 0.02–0.13 in 2013 and 2014, respectively.

### 3.3. Ammonia volatilization

The $NH_3$ volatilization flux followed a similar trend as the surface water $NH_4$-N concentrations in 2013 and 2014 (Fig. 6). The highest peak of the $NH_3$ volatilization flux were observed in the $U_b$ treatment and were 1.7–1.8 kg N $ha^{-1}$ $d^{-1}$ after application of the basal N fertilizer. Three peaks were observed in the $U_s$ treatment and were 0.8–1.4, 1.1–1.8, and 0.3–0.8 kg N $ha^{-1}$ $d^{-1}$ after application of the basal N fertilizer and two topdressings, respectively. In contrast to conventional U treatments, the $NH_3$ volatilization flux was negligible in all of the CRU treatments, except that the peak values (0.7 and 1.2 kg N $ha^{-1}$ $d^{-1}$) in response to CRU-3, but lower 33.2–55.4% than those measured in the U treatments.

Positive and significant correlations between the $NH_3$ volatilization rate and $NH_4$-N concentrations in the surface water were found among all fertilizer treatments (Table 2). The $NH_3$ volatilization rate and pH were negatively correlated in 2013 and positively correlated in 2014 but the relationships were significant only for the CK and CRU-1 treatments in 2013 and the $U_b$ and $U_s$ treatments in 2014.

The cumulative $NH_3$ volatilization loss in 2013 and 2014 was ranked as $U_b \approx U_s$ > CRU-3 > CRU-1 ≥ CRU-2 > CK (Fig. 7). Compared with the U treatments, the cumulative $NH_3$ volatilization losses in the CRU treatments were reduced by 28.9–51.3% in 2013 and 22.9–62.2% in 2014. In addition, the percentage of N loss through $NH_3$ volatilization relative to the total N fertilizer applied was 4.5–5.7 and 4.7–5.2% in the $U_b$ and $U_s$ treatments, compared with 1.1–1.3, 0.2–0.7 and 2.3–3.3% in the CRU-1, CRU-2 and CRU-3 treatments, respectively, in 2013 and 2014.

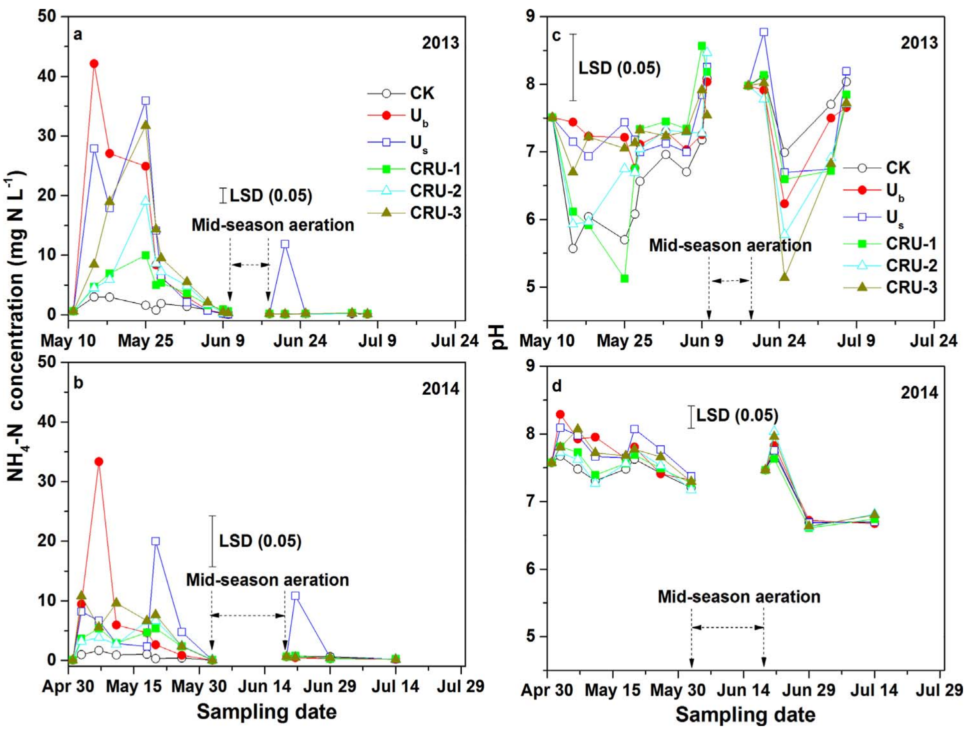


**Fig. 5.** Surface water $NH_4$-N concentration (a, b) and pH (c, d) during the 2013 and 2014 rice growing seasons. LSD (0.05) is the least significant difference among treatments in a sampling date at $P < 0.05$. Different fertilizer treatments are depicted as control with 0 kg N $ha^{-1}$ (CK), basal application of urea ($U_b$), split application of urea ($U_s$), polyurethane-coated urea (CRU-1), degradable polymer-coated urea (CRU-2) and water-based polymer-coated urea (CRU-3).

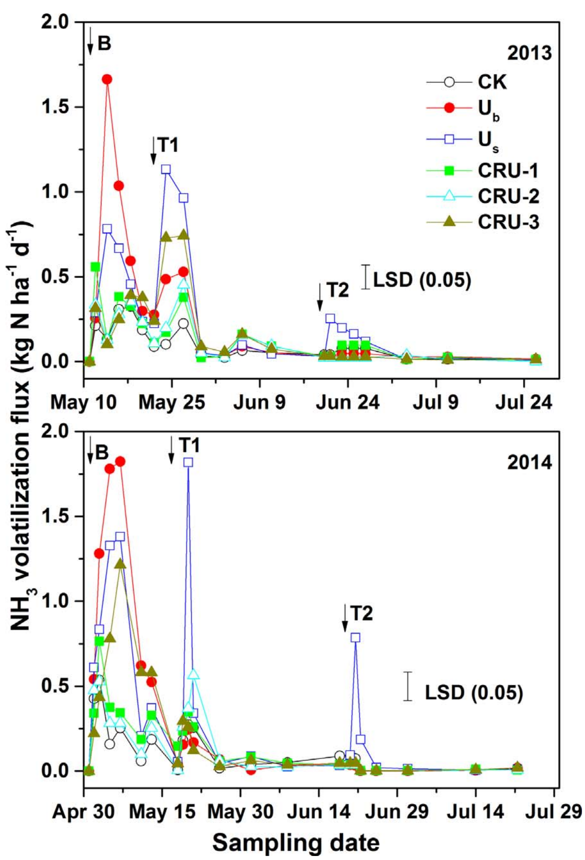


**Fig. 6.** $NH_3$ volatilization flux during the 2013 and 2014 rice growing seasons. LSD (0.05) is the least significant difference among treatments in a sampling date at $P < 0.05$. The variables B, T1 and T2 indicate the application of basal N fertilizer, the first topdressing, and the second topdressing, respectively. The treatment's description is given in Fig. 5.

**Table 2**
Pearson correlation coefficients between $NH_3$ volatilization rate and surface water properties ($NH_4$-N concentration and pH), and between mineral N surface runoff and precipitation during the 2013 and 2014 rice growing seasons.

| Treatment[a] | $NH_3$ volatilization | | Mineral N surface runoff |
|---|---|---|---|
| | $NH_4$-N | pH | Precipitation |
| 2013 (n = 21)[b] | | | |
| CK | 0.608* | −0.652* | 0.855** |
| $U_b$ | 0.928** | −0.107 | 0.785* |
| $U_s$ | 0.906** | −0.142 | 0.673 |
| CRU-1 | 0.580* | −0.548* | 0.796* |
| CRU-2 | 0.540* | −0.421 | 0.764* |
| CRU-3 | 0.867** | −0.059 | 0.751* |
| 2014 (n = 22) | | | |
| CK | 0.410 | 0.482 | 0.968** |
| $U_b$ | 0.916** | 0.603* | 0.744 |
| Us | 0.897** | 0.658* | 0.865* |
| CRU-1 | 0.663* | 0.541 | 0.824* |
| CRU-2 | 0.520 | 0.416 | 0.836* |
| CRU-3 | 0.568 | 0.532 | 0.788* |

[a] CK, 0 kg N $ha^{-1}$; U, urea ($U_b$, basal application of urea; $U_s$, split application of urea); CRU, controlled-release urea (CRU-1, polyurethane-coated urea; CRU-2, degradable polymer-coated urea; CRU-3, water-based polymer-coated urea).
[b] Sample number in the parentheses.
* Significant at 0.05 probability level.
** Significant at 0.01 probability level.

### 3.4. Nitrogen surface runoff

During the 2013 and 2014 rice growing seasons, 8 and 6 surface runoff events occurred, respectively (Fig. 8). The order of the total mineral N surface runoff in the different fertilization treatments was CRU-3 > $U_s$ > $U_b$ > CRU-2 > CRU-1 > CK in 2013 and CRU-3 > $U_b$ > $U_s$ > CRU-2 > CRU-1 > CK in 2014. When compared with U treatments, the total mineral N surface runoff from the CRU treatments (except for CRU-3) were decreased by 37.7–58.3 and 7.6–22.4% in 2013 and 2014, respectively. The N loss due to the former three surface runoff events accounted for 93.7–98.6 and 57.7–94.0% of the total mineral N surface runoff loss in 2013 and 2014, respectively.

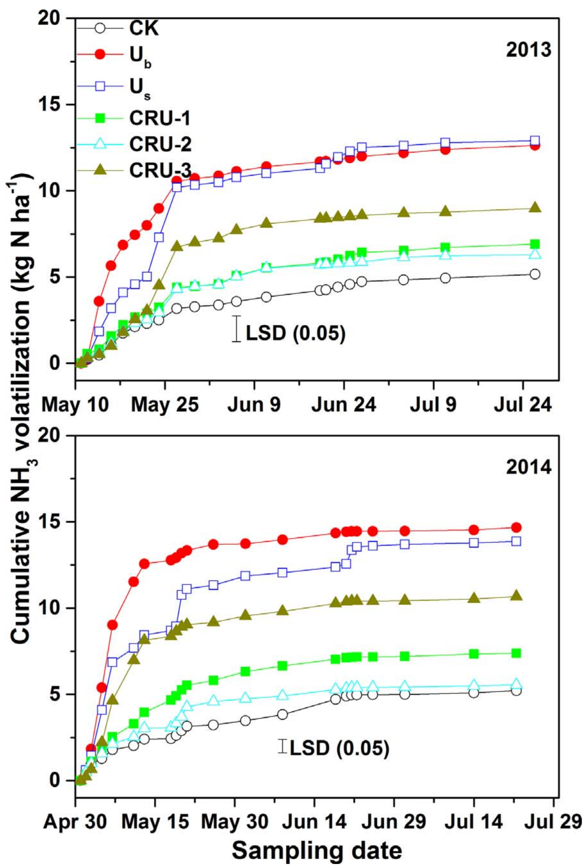


**Fig. 7.** Cumulative $NH_3$ volatilization during the 2013 and 2014 rice growing seasons. LSD (0.05) is the least significant difference among treatments in a sampling date at $P < 0.05$. The treatment's description is given in Fig. 5.

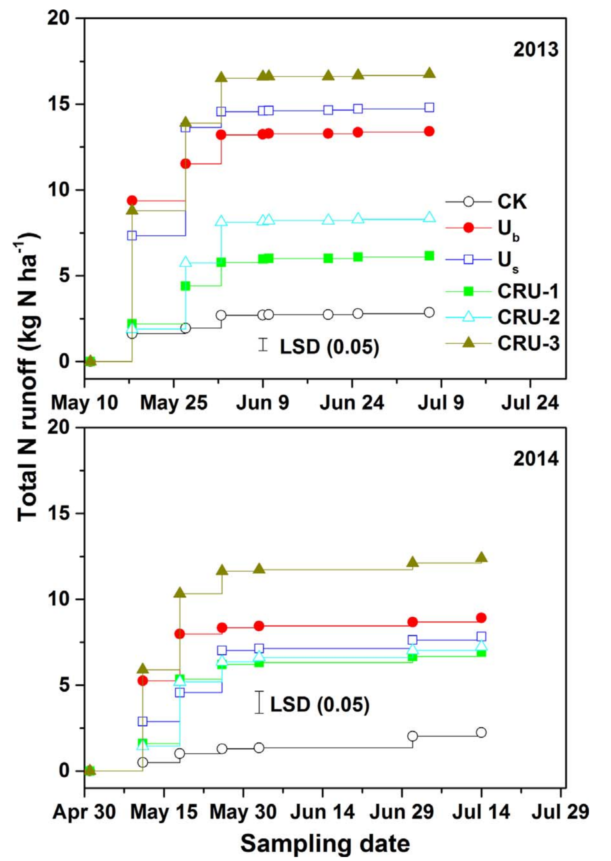


**Fig. 8.** Nitrogen surface runoff loss during the 2013 and 2014 rice growing seasons. LSD (0.05) is the least significant difference among treatments in a sampling date at $P < 0.05$. The treatment's description is given in Fig. 5.

Positive and significant correlations between the mineral N surface runoff loss and precipitation existed among all fertilizer treatments (Table 2).

### 3.5. *Grain yield, nitrogen uptake and N use efficiency*

Nitrogen fertilization treatments influenced the grain yield, N uptake and NUE (Table 3). In 2013, there were no significant differences in grain yield with the CRU and $U_b$ treatments, whereas the yields with the CRU treatments were 5.1–9.0% higher than those of the $U_s$ treatment. In 2014, the grain yield with the CRU-1 treatment was significantly higher than that measured with the $U_b$ and $U_s$ treatments, i.e., by 15.7 and 14.5%, respectively, followed by the CRU-3 (8.9 and 7.7% higher) and CRU-2 treatments (3.8 and 2.7% higher). Relative to the $U_b$ and $U_s$ treatments, the total N uptake in the CRU treatments increased by 14.9–48.8 and 8.2–40.1% in 2013 and 35.4–55.1 and 3.4–18.4% in 2014; the NUE of the CRU treatments increased by 10.3–33.6 and 6.0–29.3% in 2013 and 21.9–34.1 and 2.7–14.9% in 2014.

**Table 3**
Grain yield, total N uptake by rice plants and N use efficiency during the 2013 and 2014 rice growing seasons.

| Year | Treatment[a] | Grain Yield (t ha$^{-1}$) | Total N uptake (kg ha$^{-1}$) | N use efficiency (%) |
|---|---|---|---|---|
| 2013 | CK | 4.37 ± 0.26 c‡ | 63.7 ± 7.6 d | – |
| | $U_b$ | 7.27 ± 0.19 a | 113.5 ± 3.8 c | 30.1 |
| | $U_s$ | 6.73 ± 0.25 b | 120.5 ± 3.7 bc | 34.4 |
| | CRU-1 | 7.33 ± 0.30 a | 154.1 ± 19.5 a | 54.7 |
| | CRU-2 | 7.23 ± 0.21 a | 168.9 ± 9.7 a | 63.7 |
| | CRU-3 | 7.06 ± 0.24 ab | 130.4 ± 5.2 b | 40.4 |
| | LSD (0.05) | 0.47 | 14.9 | – |
| 2014 | CK | 3.72 ± 0.22 c | 57.8 ± 2.8 d | – |
| | $U_b$ | 6.79 ± 0.34 b | 102.0 ± 11.4 c | 26.8 |
| | $U_s$ | 6.87 ± 0.46 b | 133.6 ± 7.1 b | 46.0 |
| | CRU-1 | 7.86 ± 0.42 a | 158.2 ± 15.8 a | 60.9 |
| | CRU-2 | 7.05 ± 0.43 b | 144.8 ± 13.0 ab | 52.7 |
| | CRU-3 | 7.40 ± 0.40 ab | 138.1 ± 13.7 ab | 48.7 |
| | LSD (0.05) | 0.73 | 22.7 | – |

Data are presented as means ± standard deviation of three replicates. Means followed by different letters in columns are significantly different at $P < 0.05$ by LSD.

[a] CK, 0 kg N ha$^{-1}$; U, urea ($U_b$, basal application of urea; $U_s$, split application of urea); CRU, controlled-release urea (CRU-1, polyurethane-coated urea; CRU-2, degradable polymer-coated urea; CRU-3, water-based polymer-coated urea).

## 4. Discussion

### 4.1. *Effects of different CRU fertilizers on $NH_3$ volatilization and N surface runoff losses*

Previous studies showed that the vented-chamber method was suitable for in situ assessment of the exact loss of $NH_3$ from surface to the atmosphere due to its higher precision and accuracy, it is easy to operate, and their results are similar to micrometeorological and wind tunnel methods (Der Weerden et al., 1996; Zhu and Wen, 1992; Wang et al., 2004). The average cumulative $NH_3$ volatilization occurred in U and CRU treatments were 12.8 and 7.4 kg N ha$^{-1}$ (4.6 and 1.3% of the applied N) in 2013 and 14.3 and 7.9 kg N ha$^{-1}$ (5.5 and 1.6% of the applied N) in 2014, respectively (Fig. 7). Based on the approximate amounts of N fertilizer application, the seasonal $NH_3$ volatilization was slightly lower than that previously reported for Chinese rice paddies (Xu et al., 2012; Shang et al., 2014). One possible reason may be differences in the methodology used for measurements. A continuous

ventilation method using a PVC tube (which has been used to measure $NH_3$ volatilization in maize and wheat fields) possibly leads to an underestimation of the actual flux (Wang et al., 2004). Other reasons may be different crop growth periods (single or double rice cropping) and environmental conditions such as soil pH, meteorological conditions and surface water properties.

The $NH_3$ volatilization fluctuates strongly with meteorological conditions (Xu et al., 2012; Yang et al., 2013b), especially temperature and precipitation. During the measurement periods, $NH_3$ volatilization reached a peak that occurred later under conditions of low temperature and high precipitation, i.e., 6–8 d after B compared with 2–3 d under hot and low precipitation conditions. Precipitation (16.5 mm) and low temperature (17.6 °C) on the 3rd day in 2014 delayed the peak $NH_3$ volatilization by 3 d compared to conditions with no precipitation and high temperature (25.2 °C), a time when emissions peaked on the 3rd day. In early rice growing season, the high frequency of precipitation and low temperature restricted $NH_3$ volatilization loss, especially when precipitation occurred after fertilization. Instead, the high temperature and low frequency of precipitation promoted $NH_3$ volatilization loss in late rice growing season (Li et al., 2017a). These findings indicate that changes in air temperature and precipitation may influence the $NH_3$ volatilization rate and that the risk of $NH_3$ volatilization loss may increase with an increase in temperature and after precipitation. Chen et al. (2015) suggested that air temperature alters $NH_3$ volatilization by affecting the temperature of surface water, with precipitation affecting $NH_3$ volatilization by altering the $NH_4^+$-N concentration and pH of surface water after urea application. In comparison with the U treatments, $NH_3$ volatilization losses in the CRU treatments were not significantly affected by climatic conditions because the N release rate from the CRU was much slower than that from conventional urea (Yang et al., 2013a). The relationships between $NH_3$ volatilization and surface water properties ($NH_4^+$-N concentration and pH) suggested that the $NH_4^+$ concentration is a predominant factor defining $NH_3$ volatilization in rice paddies (Figs. 5 a, b, 6 and Table 2), which is consistent with previous reports (Xu et al., 2012; Shang et al., 2014). CRU (except for CRU-3) significantly decreased TN loss through surface runoff in 2013 and 2014. These results are consistent with those of Yang et al. (2015), who found that CRU significantly reduced TN loss through surface runoff by 72.5 and 47.8% in 2009 and 2010, respectively, compared with a conventional farmer's fertilization practice.

### 4.2. Effects of different CRU fertilizers on grain yield and N use efficiency

Several CRU products and application methods have been applied for enhancing crop yields and NUE as well as minimizing N losses (Kiran et al., 2010; Connell et al., 2011). Yang et al. (2013a,b) reported that CRU improved NUE and rice yield, and reduced environmental risks. However, there is substantial variability in the reported benefits of CRU with regard to increasing crop yield and NUE (Golden et al., 2009; Blackshaw et al., 2011; Li et al., 2017a). Thus, the potential of CRU should consider the environmental conditions in a given region (Grant et al., 2012).

In this study, minor yield losses occurred in the CRU-1 and CRU-2 treatments compared with the $U_b$ treatment due to slow release of CRU, which impaired the early-season N availability and crop growth. However, the NUE values obtained with CRU in 2013 and 2014 were 40.6-63.6% and 57.3-70.7% higher than those with urea, respectively (Table 3). Similar results were reported by Golden et al. (2009), who reported that NUE from urea in split applications were 12–15% lower than those for single basal applications of CRU. According to Yang et al. (2012), the NUE values in response to CRU applied at a rate of 300 kg N $ha^{-1}$ were 27.6 and 22.9% higher than those for conventional urea in 2007 and 2008, respectively. Fageria and Carvalho (2014) also reported an increase (approximately 25%) in NUE with polymer-coated urea compared with conventional urea. In the late rice growing season, CRU treatments also increased NUE by 2.7–17.4 percentage point compared with conventional urea (Li et al., 2017a). The results suggest that the grain yield with CRU could equal or even surpass that with $U_s$, while reducing the number of topdressing applications and saving labor to achieve better economic and environmental benefits.

### 4.3. Nitrogen release of controlled-release urea

Polymer-coated urea fertilizers are considered to be the most promising CRU due to their superior release rate, greater potential release of nutrients corresponding to the nutrient demands of crops, and greater environmental and economic benefits (Du et al., 2006). However, the benefits of CRU were affected by the characteristic of coated materials, and environmental factors such as soil temperature and moisture (Grant et al., 2012; Ke et al., 2017). In this study, a typical rapid release behavior was observed for CRU-1 and CRU-2 during the first 30 d (Fig. 4). This is coincident with the fertilizer uptake characteristics of early rice in a double rice cropping system because large amounts of N are needed after early rice transplanting, with an evident peak in N absorption (Xi et al., 1978). CRU-3 released approximately 80% of the N during the first 10 d, which might be attributed to the fact that this product is limited by the hydrophilicity of its water-soluble polymer, resulting in a short release duration. Therefore, the practices of CRU-3 application to early rice in double rice cropping system may have to be improved, though further investigation is required (Zhao et al., 2010). Higher precipitation and air temperature in 2014 compared to 2013 were the main reasons for inter-annual variations of N release pattern of CRU (Figs. 2 and 4), which promotes N release rate. Consistent results were observed for $NH_3$ volatilization and N surface runoff, which were consistent with previous reports (Ke et al., 2017).

There were significantly differences in temperature and rainfall between early rice and late rice which had obvious effects on CRU. The early rice growing season extends from April to July and corresponds with the plum rain period in the middle and lower reaches of Yangtze River, and it is often subjected to heavy rainfall and low temperature weather conditions after fertilization, whereas less rainfall and high temperature occur in the late rice growing season (Shen et al., 2011; Wu et al., 2013; Li et al., 2017a). Moreover, the benefits of CRU are affected by soil temperature and moisture (Grant et al., 2012; Ke et al., 2017). The agronomic and environmental performances of CRU in production of early rice and late rice vary significantly. Hence, it was necessary to separately evaluate the performance of CRU in early rice and late rice.

### 4.4. Significance of the soil system in sustainable agriculture

The sustainability of human societies depends on sustainable agriculture (Keesstra et al., 2016). However, the agricultural sustainability is currently facing enormous challenges at local, national and global scales (Zhang et al., 2015; Li et al., 2017b). Agricultural practices not only determine crop productivity, but also largely influence the global environmental quality (Tilman et al., 2002). Soils provide us with basic human needs like food, fresh air, and clean air (Keesstra et al., 2016). However, high intensity use of soils usually leads to poor soil functioning such as soil erosion, nutrients losses through runoff and leaching, eutrophication and salinization, etc., resulting in many environmental problems (Mol et al., 2012). Soil management has important effects on soil properties, soil erosion, soil losses and soil quality (Parras-Alcantara et al., 2016). One of the most effective tactics to sustain crop productivity while reducing environmental risk in sustainable agriculture is improving NUE. Recently, NUE, as a positive indicator, has been proposed to assess progress in achieving the Sustainable Development Goals of the United Nations (Zhang et al., 2015). This study showed that CRU significantly improved NUE and reduced N losses through volatilization and surface runoff, which is of great significance to realize the United Nations' Sustainable Development Goals.

## 5. Conclusions

Precipitation and the $NH_4^+$-N concentration in surface water were the predominant factors affecting N losses through $NH_3$ volatilization and surface runoff. The N release characteristics of two of the three CRU fertilizers evaluated were able to fulfill the nutrient demand of rice plants throughout the entire early rice season. Compared with U treatments, application of CRU mitigated $NH_3$ volatilization and mineral N surface runoff losses under rice while supplying an equivalent amount of N needed to produce the optimum yield. Application of CRU may also decrease the $NH_4$-N concentration and pH of surface water. Compared to conventional urea fertilizer, application of CRU could maintain or even increase grain yields, N uptake by rice plants and NUE, though the magnitude of these benefits will vary according to the characteristics of different CRU fertilizers. Overall, CRU-1 proved suitable to be used in early rice in the double rice cropping system in southern China.

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